

Durable Zinc-Oxide-Containing Regenerable Desulfurization Sorbents for Both Low- and High-Temperature Applications

by

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Abstract

A regenerable desulfurization sorbent, developed by researchers at the U.S. Department of Energy's (DOE's) Federal Energy Technology Center (FETC), has demonstrated very high attrition resistance and stable reactivity under numerous testing regimes in both simulated and actual fuel gas conditions. This sorbent, identified as RVS-1 (formerly METC-10), is suitable for applications in a wide range of temperatures (260-600 °C (500-1100 °F)). This sorbent is commercially available from United Catalysts Inc. (UCI). The moving/fixed-bed version of this sorbent exceeded all stringent performance criteria required for use in the Tampa Electric Company Clean Coal Technology (TECO/CCT) electric power generation plant. The sorbent has a high sulfur capacity of 17-20 wt % demonstrated during multiple cycle tests while maintaining the H₂S level below 5 ppm. Mechanical strength and attrition resistance of the sorbent remained stable or improved during multiple cycle tests. Effects of temperature, pressure, and H₂S concentration on the sorbent performance were examined. Concentration of H₂S in the gas stream had a major effect on the sulfur capacity of the sorbent at both low pressures and low temperatures. This is theorized to be due to diffusional resistance inside the pores of the sorbent pellet. Even at low temperature (260 °C (500 °F)), it was possible to achieve a sulfur loading of 17 wt %, indicating that the sorbent is suitable for applications over a wide range of temperatures. At low pressures, high sulfur loading (>17 wt %) was achieved at low H₂S concentrations (~2,000 ppm) while at high pressure (>1,136 kPa), high sulfur loading was achieved even

with a high H_2S concentration (2%). The sorbent is suitable for sulfur removal from gas streams with both low and high reducing power. The sorbent can be easily regenerated at 482 °C (900 °F) with oxygen. Presence of steam during regeneration does not affect the sorbent performance. In addition to H_2S , the sorbent is also capable of absorbing other sulfur compounds, such as dimethyl sulfide and carbonyl sulfide. It was also possible to prepare the RVS-1 sorbent to be suitable for fluidized/transport reactor bed applications using a spray drying technique. It was also possible to achieve sulfur efficiencies in the ppb range with the modified RVS1 sorbent.

1. Introduction

Development of a suitable regenerable sorbent is one of the major barrier issues in the gas cleanup program for Integrated Gasification Combined-Cycle (IGCC) systems. A series of novel sorbents containing zinc oxide were developed at FETC to address these problems (Siriwardane 1998). These FETC-developed sorbents showed excellent performance during 20-cycle high-pressure fixed-bed tests with steam regeneration, and a 50-cycle high-pressure fixed-bed test with dry regeneration. In addition, one of the sorbents (RVS-1) was tested in the moving bed reactor at the General Electric (GE) pilot plant. Despite several operational problems at the facility, promising results were obtained during the testing. The RVS-1 sorbent was tested in a fixed bed for 25 sulfidation/regeneration cycles at Research Triangle Institute (RTI) under regeneration conditions that closely simulated those encountered at the TECO/CCT project (Siriwardane et al. 1998). The performance of the sorbent was excellent under these conditions, and it exceeded all the performance criteria required for the TECO/CCT project. The RVS-1 sorbent was tested at lower temperatures to determine whether it was suitable for low-temperature applications (Siriwardane 1998). The sorbent had an excellent sulfur capacity, even at 260 °C (500 °F).

A systematic study to understand the effect of temperature, pressure, gas composition, and H_2S concentration on the performance of RVS-1 sorbent was conducted, and the results of this study are discussed in this paper. In addition, a sorbent suitable for use in fluidized/transport reactor beds (RVS-2) was also tested in a bench-scale reactor. Reasonable attrition and sulfur capacity values were obtained for these sorbents. These promising results are also discussed in this paper.

2. Experimental

The RVS-1 sorbent was developed by FETC in-house researchers. UCI prepared the RVS-1 sorbent under guidance from FETC using equipment large enough to produce a sorbent batch with the physical and chemical characteristics that would be obtained for a commercially prepared sorbent batch. This sorbent was supplied as 3-mm ellipsoidal pellets. The RVS-1 sorbent is commercially available from UCI.

The fixed-bed tests were conducted at RTI. Sulfidations were performed at both 538 °C (1,000 °F) and 260 °C (500 °F) using simulated TECO coal gas (35.8% CO , 12.2% CO_2 , 26.8% H_2 , 18.1% steam, and 5.95% nitrogen). The pressures during sulfidations were 239, 1,136, and 2,032 kPa (2.4, 11.2, and 20 atm). Regeneration was performed at 239 kPa (2.4 atm) with 3.5% O_2 at 566 °C (1,050 °F). Space velocity during sulfidation and regeneration was 2,000 hr^{-1} . Two and half cycle tests were conducted, and physical and chemical characteristics of the solid samples were determined after the third sulfidation. The sorbent was

loaded up to 6.7 lb/ft³ during sulfidations, but the last sulfidation cycle was conducted until the breakthrough (200 ppm H₂S). LECO sulfur analysis and X-ray photoelectron spectroscopy (XPS) were conducted to determine the total sulfur uptake and sulfur species at the surface of the samples, respectively, after sulfidations.

RVS-2 sorbent suitable for fluid/transport reactor-bed testing was prepared using a spray drying technique. This sorbent was tested in a bench-scale low-pressure fluid-bed reactor. Sulfidations were performed at 538 °C (1,000 °F) and 239 kPa (2.4 atm) using simulated KRW coal gas (47% nitrogen, 8% steam, 5% CO₂, 24% CO, and 14% H₂) with 2% H₂S. The superficial gas velocity for all sulfidations was 4.75 cm/sec. The outlet H₂S was monitored using on-line mass spectrometry and gas chromatography. All dry regenerations in the low-pressure reactor were done at 239 kPa (2.4 atm) with 6% oxygen in nitrogen at 538 °C (1,000 °F). The sorbent was loaded up to 6.7 lb/ft³ during sulfidations, but the last sulfidation cycle was conducted until the breakthrough.

3. Results and Discussion

3.1 *Effect of H₂S Concentration on Sulfidation (Fixed-Bed Reactor Tests)*

The breakthrough (200 ppm H₂S) times for the third sulfidation and the calculated sulfur loading values at the breakthrough with varying H₂S concentrations at 20 psig are shown in Table 1. It is interesting to see that the concentration of the inlet gas has a major effect on the breakthrough time at 239 kPa.

Table 1
Breakthrough Times for Third Sulfidations
and Calculated Sulfur Loading of the Reactor Bed at 239 kPa and 538 °C

H ₂ S Concentration (ppm)	Breakthrough Time (min)	Calculated Sulfur Loading of the Bed (wt%)
2,000	2,100	13.9
7,000	350	7.5
12,000	222	7.7

The measured sulfur loading values as a function of reactor bed position are shown in Figure 1. Position 10 corresponds to the gas inlet location of the reactor bed, while position 1 corresponds to the gas outlet location. It is clear that the amount of sulfur loading depends on the H₂S concentration of the inlet gas. It was possible to obtain a higher amount of sulfur at 2,000 ppm (~17 wt %) than at both 7,000 ppm and 12,000 ppm (~13 wt %). The variation in the distribution of sulfur in the reactor bed was considerably larger at both 7,000 ppm and 12,000 ppm than at 2,000 ppm. The higher sulfur loading and fairly uniform sulfur distribution in the reactor bed at 2,000 ppm is thought to be due to the lower diffusional resistance of the H₂S within the sorbent pellet.

The sulfide/zinc ratios at the surfaces of both the exterior of the pellet and the interior of the pellet (cross section) as determined by XPS are shown in Table 2. It is interesting to note that the concentration of H₂S has no significant effect on the amount of sulfide/zinc at the exterior pellet surface at all bed locations. However, the sulfide/zinc ratio at the interior of the pellets was significantly affected by the H₂S concentration. The pellets that were reacted with 12,000 ppm H₂S had considerably lower sulfide/zinc at the interior of the pellet than those that were reacted with 2,000 ppm H₂S. It appears that the initial sulfide product layer formed at the exterior surface of the pellet with higher H₂S concentration inhibits the diffusion of H₂S to the interior of the pellet. Thus, the highest utilization of the sorbent for sulfur uptake at 239 kPa can be achieved only at lower H₂S concentrations.

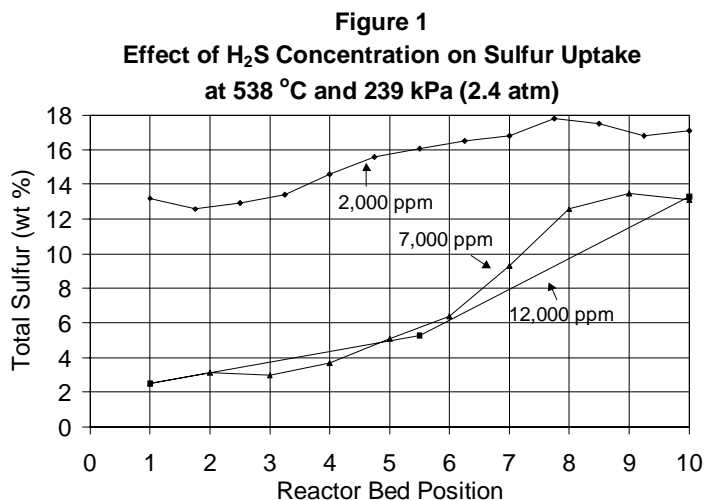


Table 2
Sulfide/Zinc Ratios with Varying H₂S Concentrations (XPS analysis)

Pellet Location/Reactor Bed Location	2,000 ppm H ₂ S	12,000 ppm H ₂ S
Exterior/Gas Outlet	0.61	0.57
Exterior/Middle	2.09	0.81
Exterior/Gas Inlet	1.89	1.84
Interior/Gas Outlet	0.47	0.00
Interior/Middle	0.46	0.17
Interior/Gas Inlet	0.96	0.42

3.2 Effect of Pressure on Sulfidation

The breakthrough times and the calculated sulfur loading values from the breakthrough curves at different pressures are shown in Table 3. The sulfur loading values measured using LECO sulfur analysis are shown in Figure 2. It is evident that the pressure has a significant effect on the sulfur uptake of these sorbent pellets. At higher pressures (1,136 and 2,032 kPa), the sulfur uptake values with 12,000 ppm H₂S are considerably higher than those at 239 kPa. This indicates that the diffusion of H₂S to the interior of the pellet is enhanced at higher pressure.

Figure 2
Effect of Pressure on Sulfur Uptake
at 538 °C with 1.2% H₂S

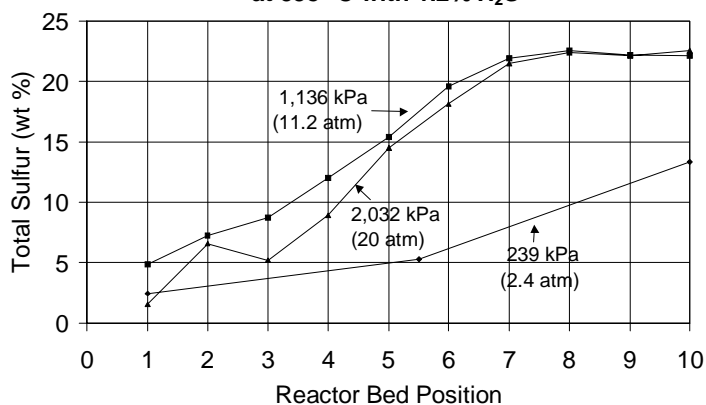


Table 3
Breakthrough Times and Calculated Sulfur Loading Values
at Different Pressures with 12,000 ppm H₂S

Pressure (kPa)	Breakthrough Time (min)	Calculated Sulfur Loading (wt%)
239	222	7.7
1,136	450	17.1
2,032	400	15.3

The sulfide/zinc ratios measured using XPS are shown in Table 4. The sulfide/zinc at the interior of the pellet is considerably higher for all samples at 1,136 kPa than at 239 kPa. This clearly demonstrates the enhanced diffusion of H₂S to the interior of the pellet at higher pressure. The sulfide/zinc ratio at the exterior of the pellet was slightly higher than that at the interior at lower pressure. It appears that at lower pressure H₂S reacts with the exterior of the pellet before diffusion to the interior of the pellet and forms a product layer which inhibits further diffusion into the pellet. At higher pressures (>1,136 kPa), the sorbent was utilized effectively even with 12,000 ppm H₂S. At lower pressure (239 kPa), the sorbent pellets were utilized effectively only at low H₂S concentration (2,000 ppm).

Table 4
XPS Data on Sulfide/Zinc ratios of Sorbent Pellets at Different Pressures

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Pellet Location/Reactor Bed Location	239 kPa	1,136 kPa
Exterior/Gas Outlet	0.50	0.31
Exterior/Middle	0.80	0.57
Exterior/Gas Inlet	1.83	1.36
Interior/Gas Outlet	0	0.24
Interior/Middle	0.16	0.67
Interior/Gas Inlet	0.42	1.88

3.3 *Effect of Temperature on Sulfidation*

The breakthrough times and calculated sulfur loading values at both 538 °C (1,000 °F) and 260 °C (500 °F) with 12,000 ppm H₂S at 2,032 kPa are shown in Table 5. The measured sulfur loading values as a function of reactor bed location are shown in Figure 3.

Table 5
Breakthrough Times and Calculated Sulfur Loading Values
at Different Temperatures with 12,000 ppm H₂S

Temperature (°C)	Breakthrough Time (min)	Calculated Sulfur Loading (g)
260	250	8.6
538	400	15.3

It is clear that the sulfur uptake is lower at 260 °C (500 °F) than at 538 °C (1,000 °F). This could either be due to the higher diffusional resistance or the lower extent of reaction at lower temperature. In order to determine whether this is due to diffusional resistance, sorbent tests were performed at 2,032 kPa and at 260 °C (500 °F) with 2,000, 7,000, and 12,000 ppm H₂S. The breakthrough times and calculated sulfur loading values are shown in Table 6 and the measured sulfur loading values are shown in Figure 4.

Figure 3
Effect of Temperature on Sulfur Uptake
at 2,032 kPa (20 atm) with 1.2% H₂S

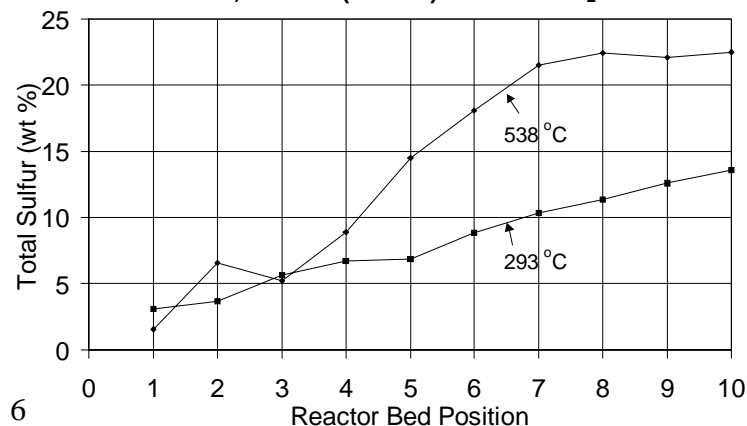


Table 6
Breakthrough Times and Calculated Sulfur Loading Values
at 260 °C (500 °F) and 2,032 kPa with Different Concentrations of H₂S

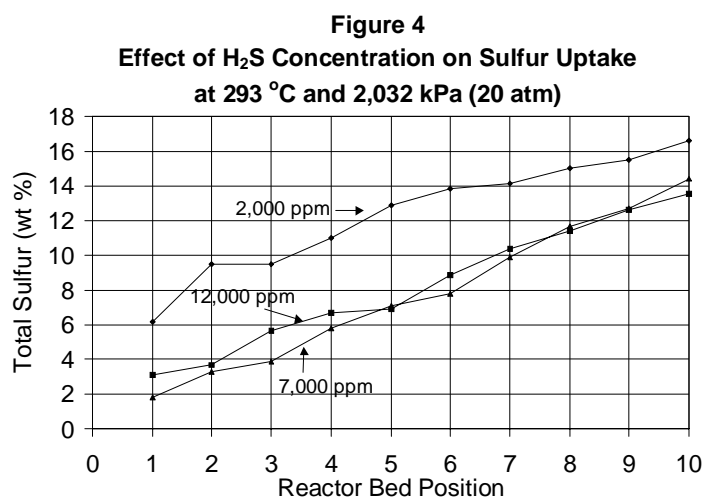
H ₂ S Concentration (ppm)	Breakthrough Time (min)	Calculated Sulfur Loading (wt %)
2,000	2,500	16.5
7,000	400	8.3
12,000	250	8.6

It is clear that at 260 °C (500 °F) and 2,032 kPa, a higher sulfur uptake can be achieved at a lower concentration of H₂S. At 538 °C (1,000 °F) the sulfur uptake was only sensitive to the H₂S concentration when the sulfidation was performed at lower pressure, but not at higher pressure (1,136 and 2,032 kPa). However, the sulfur uptake is sensitive to concentration of H₂S even at high pressure (2,032 kPa) when the sulfidation was performed at 260 °C (500 °F). The sorbent pellets were better utilized for sulfidation with 2,000 ppm of H₂S at 260 °C (500 °F), and it was possible to achieve a sulfur loading of 17 wt %. This indicates that there was a higher diffusional resistance at lower temperature when the H₂S concentration was high, but sulfur uptake similar to that at 580 °C (1,000 °F) can be achieved at 260 °C (500 °F) by lowering the H₂S concentration to 2,000 ppm.

3.4 Fluidized Bed Reactor Tests

The RVS-2 sorbent was prepared using a spray drying method. The bulk density of the sorbent was 0.96 g/cc. The Davidson attrition index value (measured at M.W. Kellogg Co.) of the sorbent was 7 wt %, indicating that the attrition resistance value of the sorbent was good. Sulfur capacity of the sorbents (measured by thermogravimetric analysis, or TGA) after 9½ cycles of testing showed total sulfur uptake of 11.3 wt %. This sulfur capacity remained unchanged during multi-cycle TGA tests. The sulfur capacity after 2½ cycles of low pressure bench scale tests was 10 wt %.

3.5 Sorbent Modification to achieve sulfur removal efficiency in the ppb range



The RVS1 sorbent was modified to obtain sulfur removal efficiency levels in the ppb range. Sulfidations were performed at 315 °C (600 °F) using simulated TECO coal gas containing 2000 ppm H₂S for the first 480 minutes of sulfidation and then the H₂S concentration was increased to 10,000 ppm. The pressure during sulfidations was 2,032 kPa (20 atm). Regeneration was performed at 239 kPa (2.4 atm) with 2 % O₂ at 677 °C (1,250 °F). Space velocity during sulfidation and regeneration was 2,000 hr⁻¹. The prebreakthrough H₂S level was around 100 ppb for 200 minutes and then it was increased to about 200 ppb until close to breakthrough (100 ppm sulfur). It was possible to maintain the H₂S removal efficiency in the ppb level after regeneration.

4. Conclusions

A regenerable desulfurization sorbent known as RVS-1 showed very promising results during multi-cycle tests. The sorbent is operational at a wide range of temperatures (260-600 °C (500-1,100 °F)) and has a high sulfur capacity of 17-20 wt % while maintaining the H₂S leak rate below 5 ppm. The operational parameters for the sorbent have been fully identified during the study. At low temperature (260 °C (500 °F)) and high pressure (>1,136 kPa), high sulfur loadings can be achieved with low H₂S concentrations (~2,000 ppm). At low pressures and high temperatures, high sulfur loading (>17 wt %) was achieved only with low H₂S concentrations (~2,000 ppm), while at high pressure (>1,136 kPa), high sulfur loading was achieved even with a high H₂S concentration (2%). This was attributed to the diffusional resistance inside the pores of the sorbent pellet. It was possible to modify the sorbent to achieve the sulfur removal efficiency in the ppb range.

5. References

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